(calcd 306.2); IR (neat) 1195 (CI), 800 (Ar H) cm^{-1}; NMR (neat) δ 1.0 (d, 3, CH$_3$), 1.6 (m, 1, CH), 2.2 (s, 3, ArCH$_3$), 2.7 (d, 2, CH$_2$I), 3.2 (d, 2, SCH$_2$), 7.0 (A'$_2$X'$_2$, 4 Ar H).

3-(3,4-(Methylenedioxy)phenyl)-1-iodopropane. Safrole (30 mmol, 4.9 g) was hydroborated with 10 mmol of BH$_3$–THF at 0 °C for 1 h. Iodination was carried out at room temperature. After 45 min, the product was isolated via chromatography: yield 4.32 g (75%); bp 105 °C (0.08 torr); m/e 290.2 (calcd 290.1); IR (neat) 1490 (C=C), 1440 (C=C), 1250 (OAr), 1210 (CI), 1040 (CH$_2$–O), 940 (ArH), 800 (ArH) cm^{-1}; NMR (neat) δ 2.0 (m, 2 H, CH$_2$), 2.6 (t, 2, CH$_2$I), 3.1 (t, 2, ArCH$_2$), 5.8 (s, 2, OCH$_2$O), 6.6 (s, 3, Ar H).

5-Chloro-1-iodopentane. 5-Chloro-1-pentene (30 mmol, 3.1 g) was hydroborated with 10 mmol of BH$_3$–THF at 0 °C for 1 h. Iodination was carried out at room temperature. After 45 min, the product was isolated via chromatography: yield 3.79 g (82%); bp 30–31 °C (0.1 torr); m/e 232.3 (calcd 232.5); IR (neat) 1300 (CCl), 1200 (CI) cm^{-1}; NMR (CDCl$_3$) δ 1.8 (m, 6, CH$_2$CH$_2$CH$_2$), 3.2 (t, 2, CH$_2$I), 3.6 (t, 2, CH$_2$Cl).

Selectivity in the Oxidation of Branched Alkenes by Thallic Salts[1]

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The effects of structure, temperature, and reaction medium on the selectivity of the oxidation of branched alkenes by thallic salts has been investigated. With increasing temperature the quantity of ketones decreases in the case of the oxidation of internal alkenes, while in the case of the oxidation of R^{1}R^{2}C=CH$_2$ alkenes the quantity of carbonyl compounds increases. The isoselective temperature for oxidation of internal alkenes has been found, and for R^{1}R^{2}C=CH$_2$ alkenes "inverse selectivity temperatures" have been determined. By use of the linear free-energy relationship, separation of the polar and steric effects has been carried out; it was found that steric effects had an influence on the ratio of ketone and aldehyde formation in the oxidation of R^{1}R^{2}C=CH$_2$ alkenes in an aqueous medium, while in a methanolic medium polar effects were decisive. Polar effects were also decisive in determining the ratio of carbonyl compounds and diols in the oxidation of both types of branched alkenes. The total yield of carbonyl compounds is higher for oxidation in aqueous medium.

The pyrolysis of gasoline to ethylene and propylene appears to be an attractive base process for production of carbonyl compounds. By oligomerization of its components it is possible to obtain branched alkenes and by their oxidation branched and unbranched ketones and aldehydes.

In the case of branched alkenes, their oxidation by palladium(II) salts (Wacker process) is complicated with fast isomerization of the alkene and, in addition, with formation of relatively stable π complexes of branched alkenes with palladium(II) salts.[2] The relatively high redox potential of thallic salts provides an advantage for oxidation, allowing faster product formation without isomerization of double bonds.[3]

Two characteristic products are formed by the oxidation of alkenes by thallic salts. One, invariably, was a vicinal diol, with the carbon skeleton of the starting alkene, and the other was a carbonyl compound (aldehyde and/or ketone) whose character was given by the structure of the starting alkene. By oxidation of terminal n-alkenes only ketones are formed[4] and in the case of internal alkenes

isomeric ketones.[5] In the oxidation of R^{1}R^{2}C=CH$_2$ alkenes the significant difference is the fact that an aldehyde is formed as well.[6]

More recently we discovered an important effect of medium and structure on the selectivity of the oxidation of terminal n-alkenes.[7] In the case of branched alkenes a more complete study of the effects of experimental conditions and structure on selectivity has been lacking so far. This is the aim of this paper.

Experimental Section

Materials. The oxidation solution of thallium(III) sulfate was prepared as described previously.[8] The thallium concentration was determined by titrating the iodine liberated by reaction of Tl^{3+} with KI with a defined solution of Na$_2$S$_2$O$_3$.[9]

(1) Part VII in the series "Extrathermodynamic Free Energy Relationships in the Oxidation of Alkenes by Thallic Salts". Part VI: M. Strašák and J. Majer, *Collect. Czech. Chem. Commun.*, in press.

(2) J. Urbanec, M. Hrušovský, and M. Strašák, *Petrochemia*, 16, 132 (1976).

(3) M. Strašák, Ph.D. Thesis, Slovak Technical University, Bratislava, Czechoslovakia, 1976.

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(7) (a) M. Strašák and M. Hrušovský, *J. Org. Chem.*, 42, 685 (1977); (b) M. Strašák and J. Majer, *Tetrahedron Lett.*, 5037 (1978).

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Table I. Effect of Temperature on the Distribution of Carbonyl Compounds
in the Oxidation of $R^1R^2C=CH_2$ Alkenes $(X_k/X_a)^a$

no.	alkene	temperature, °C						
		10	15	20	30	40	60	80
1	isobutene		0.18 (0.81)			0.18 (0.60)		
2	2MB1	1.30 (1.32)	1.28 (1.40)	1.25 (1.50)	1.22 (1.92)			
3	2MP1	0.27 (0.41)		0.26 (0.45)	0.24 (0.57)	0.27 (0.65)		
4	244TMP1			7.46 (2.79)		4.95 (3.34)	0.67 (7.16)	0.44 (10.35)
5	2EH1			1.08 (1.90)		1.18 (2.55)	1.05 (3.91)	1.06 (4.74)
6	αMS			(1.84)		(2.59)	(3.44)	(4.25)

^{a} X_k, X_a, X_c, X_d represent the mole fractions of ketone(s), aldehyde, carbonyl compounds (i.e., sum of aldehyde and ketones), and diol or diether, respectively. The values in parentheses are for X_c/X_d.

Alkenes and standards for GC/MS were prepared as previously reported.[7a]

The other chemicals used were commercial products of reagent grade purity (Lachema, Brno).

Analysis of the Oxidation Products. For the identification of the oxidation products and the determination of their proportion, the experiments were carried out at a relatively high initial concentration of thallic sulfate; the standard conditions were as follows: 150 mL of a solution of $Tl_2(SO_4)_3$ consisting of Tl^{3+} in a concentration of 0.370 mol of Tl^{3+}/L, 20 mL of an alkene (C_8 and α-methylstyrene) or 10 mL of an alkene (C_5 and C_6), i.e., about 2 mol of an alkene/mol of Tl^{3+}, and 1.254 M H_2SO_4. Reactions were conducted in thermostated water baths (±0.1 °C). The procedure was described in our previous work.[8]

The diols formed were determined quantitatively by the periodate method.[10] The other organic products were determined by GC/MS analysis.

Gas Chromatography. The oxidation products of isobutene (IB), 2-methyl-1-butene (2MB1), 2-methyl-1-pentene (2MP1), and 2-ethyl-1-hexene (2EH1) were determined with a Chrom II apparatus (Laboratory Instruments, Prague) with a capillary column 50-m long (packed with SE) and a flame-ionization detector (sensitivity 1/10). A constant temperature of 90 °C (oxidation of IB, 2MB1, and 2MP1) or 140 °C (oxidation of 2EH1) was maintained.

The oxidation products of 2,4,4-trimethyl-1-pentene (244TMP1) and internal alkenes were determined with a Fractovap 2300 apparatus (Carlo Erba, Milano): 250 cm × 2 mm diameter column packed with 10% poly(ethylene glycol adipate) on Chromatone NAW-DMCS, temperature of the feeder 175 °C, temperature of the column 120 °C, sensitivity 1/3.2, feed stock 0.1 L.

The oxidation products of α-methylstyrene (αMS) were identified with a Hewlett-Packard 5830A apparatus using a column 1.5 m long packed with SE-coated (3%) Chromatone NAW-DMCS, a flame ionization detector, and a constant temperature of 140 °C; the temperature of the feedstock was 194 °C.

Mass Spectroscopy. A MAT 111 Gnom apparatus (Varian) with a 3-m column packed with SE-coated (3%) Chromosorb WHP was used. The feed temperature was 190 °C; the temperature program (8 °C/min) was in the range 80–300 °C. The temperature of the ion source was 225 °C, the flow rate of He 15 mL/min, the ionization voltage 80 eV, and the current intensity 270 mA. The spectra of the individual samples were compared with those of authentic compounds.

Results and Discussion

The reaction mechanism of the oxidation of alkenes by thallic salts involves three steps.[3,4,6a] The first step is the formation of a π complex by an electrophilic attack of the Tl^{3+} ion on the double bond of the alkene. The second one is the change of the π complex into a σ complex, which is the rate-determining step of the oxidation, and the latter is a product of the decomposition of the oxythallic adduct (σ complex) by solvent nucleophilic attack. This is the product-determining step of the oxidation. Decomposition is initiated by splitting off of the Tl^+-like good leaving group. During the formation of the carbonyl compounds,

(10) G. O. Curme, "Glycols", Reinhold, New York, 1952, p 337.

1,2-migration of hydride as well as alkyl and aryl groups to the carbon atom to which the OX is attached has been observed (eq 1a,b). Simultaneously with intramolecular

$$R^1COCH_2R^2 + R^2COCH_2R^1 + Tl^+ + X^+ \quad (1a)$$

$$R^1R^2CHCHO \quad Tl^+ + X^+ \quad (1b)$$
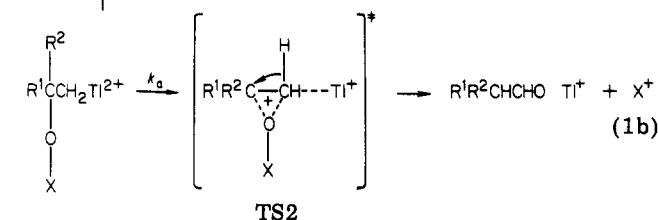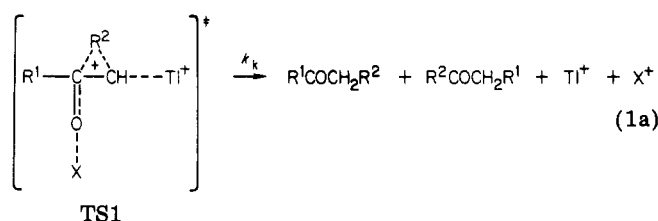
rearrangements, the nucleophilic attack by the solvent molecule occurs, and the other typical oxidation product, the vicinal diol (diether), is formed with the preserved structure of the skeleton of the starting alkene[11] (eq 2).

$$R^1R^2CCH_2OX + Tl^+ + H^+ \quad (2)$$
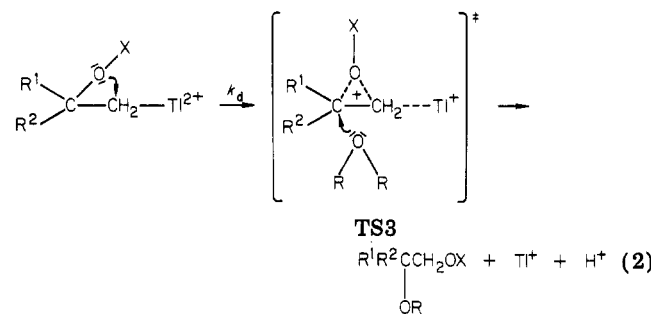
This is the case when a compound satisfying the structural assumption for a given empirical relationship undergoes competitive reactions of the same order as the intermediate oxythallic adduct. Then, according to absolute rate theory,[12] and if the reaction products are stable and do not interconvert, their relative yields represent directly the relative rates of the competing reactions. Therefore, the selectivity may be obtained from product analysis and eq 3.[13] This provides a method of obtaining

$$S = \log (k_1/k_2) = \log (X_1/X_2) \quad (3)$$

(11) C. Beaudry and M. Zador, *J. Organomet. Chem.*, **102**, 265 (1975).
(12) See for example: (a) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p 162; (b) J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions", E. S. Lewis, Ed., 3rd ed., Wiley-Interscience, New York, 1974, Part I, p 158.
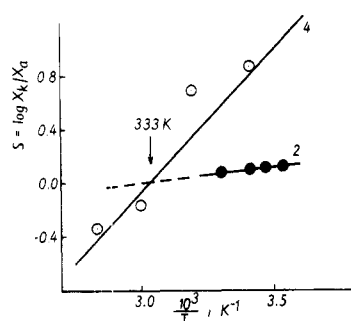
Table II. Effect of Temperature on the Distribution of the Products of the Oxidation of Internal Alkenes (X_k/X_d)

		temperature, °C							
no.	alkene	10	20	30	40	45	50	60	80
7	2MP2	12.02	6.52	4.00	2.44		1.59		
8	t4MP2		9.20	6.04	4.65	3.81			
9	244TMP2	7.50	7.00		6.46			5.94	5.94

Table III. Values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ for Oxidation of Branched Alkenes by $Tl_2(SO_4)_3$ in Aqueous H_2SO_4

no.	$\Delta\Delta H^{\ddagger},^a$ kcal/mol	$\Delta\Delta S^{\ddagger},^b$ eu
1	-2.20 ± 0.02	-0.24 ± 0.02
2	2.67 ± 0.04	-0.46 ± 0.02
	(-1.10 ± 0.08)	(0.59 ± 0.02)
3	3.27 ± 0.05	-1.22 ± 0.02
4	4.68 ± 0.32	-1.10 ± 0.02
	(-10.52 ± 1.61)	(5.17 ± 0.04)
5	3.40 ± 0.04	-0.78 ± 0.01
6	3.07 ± 0.05	-0.73 ± 0.01
7	-9.29 ± 0.04	-5.12 ± 0.03
8	-5.95 ± 0.08	-5.17 ± 0.02
9	-0.80 ± 0.02	-4.02 ± 0.03

^{a} $\Delta\Delta H^{\ddagger} = \Delta H_c^{\ddagger} - \Delta H_d^{\ddagger}$ or $\Delta\Delta H^{\ddagger} = \Delta H_k^{\ddagger} - \Delta H_a^{\ddagger}$ for the values in parentheses. ^{b} The notation is the same as for enthalpy.
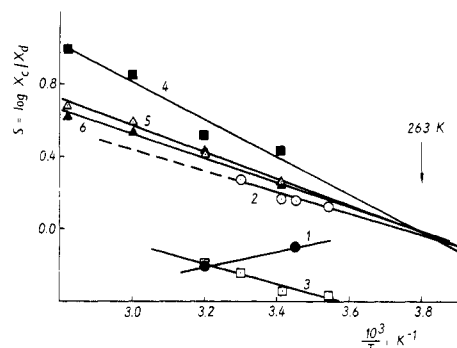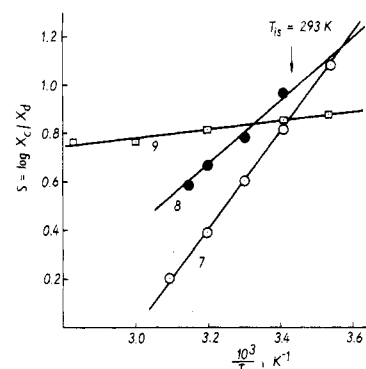

Figure 2. Plot of the selectivity (log X_c/X_d) for oxidation of $R^1R^2C{=}CH_2$ alkenes against $1/T$.

Figure 1. Plot of the selectivity (log X_k/X_a) for 244TMP1 and 2MB1 against $1/T$.

Figure 3. Effect of temperature on the selectivity (log X_c/X_d) of the oxidation of internal alkenes by $Tl_2(SO_4)_3$ in aqueous H_2SO_4.

the selectivity without the need to measure directly either relative or absolute rate constants.

Temperature Effect. The effect of temperature on selectivity for all nine substrates for oxidation by $Tl_2(SO_4)_3$ in aqueous solution is illustrated in Tables I and II. From Table I it is seen that for the ratio of the ketones to the diol, the selectivity is smallest in the case of 2EH1, while for other alkenes it is relatively high. With the exception of 244TMP1 and 2MB1 there is no marked influence of changes in temperature. For this system a plot of log (X_k/X_a) against $1/T$ gave a linear correlation as shown in Figure 1. Therefore, the selectivity of the latter two alkenes will depend on temperature according to eq 4.

$$\log (X_k/X_a) = (\Delta H_a^{\ddagger} - \Delta H_k^{\ddagger})/2.303RT - (\Delta S_a^{\ddagger} - \Delta S_k^{\ddagger})/2.303R \quad (4)$$

It is obvious that the competing reactions (the formation of ketones and aldehyde, respectively) have different activation enthalpies. From the slope $\Delta\Delta H^{\ddagger}$ and from the intersection, $\Delta\Delta S^{\ddagger}$ may be calculated. A least-squares estimate of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ was calculated, and the values are presented in Table III. From Figure 1 it may be seen that at 333 K a selectivity reversal occurs. Below this temperature more isomeric ketones are formed, while above it more aldehyde is formed. Similarly, from Figure 2 the "inverse selectivity temperature" has been found.

This is 263 K, and for oxidation in aqueous medium it has only theoretical meaning because it lies under the freezing point of water. Table I and Figure 2 show that (with the exception of isobutene) with increasing temperature the total yield of carbonyl compounds increases, while the yield of diol decreases. In the whole temperature range above 263 K carbonyl compounds (with exception of IB and 2MP1) are formed in higher yield than diols.

The temperature effect on the selectivity of the oxidation of internal alkenes is shown in Table II and Figure 3. It may be seen that with increasing temperature the total yield of ketones decreases while the yield of diol increases. This is a significant difference from the oxidation of $R^1R^2C{=}CH_2$ alkenes. The values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ calculated from the graphs in Figures 2 and 3 are given in Table III.

From Figures 1–3 it is obvious that the temperature has a drastic influence on competition reactions 1 and 2. In the oxidation of internal alkenes the selectivities of individual molecules become equal in a narrow temperature range, the isoselective temperature being represented as T_{is}. In the immediate vicinity of T_{is} the boundary condition is $S = 0$, and eq 4 can be rewritten as the isoselective relationship of eq 5.[14] Above and below T_{is} the order of

$$\Delta\Delta H^{\ddagger} = T_{is}\Delta\Delta S^{\ddagger} \quad (5)$$

(13) A. Pross, *Adv. Phys. Org. Chem.*, 14, 69 (1977).

(14) For an extensive account of the application of the isoselective relationship, see B. Giese, *Angew. Chem., Int. Ed. Engl.*, 16, 125 (1977).

Table IV. Regression Analysis

	$S = \Delta\rho^*\Sigma\sigma^* + a$				$S = \Delta\delta\Sigma E_s' + b$			
	$\Delta\rho^{*a}$	a^b	r_{xy}	$S, \%$	$\Delta\delta^c$	b^b	r_{xy}	$S, \%$
$R^1R^2C{=}CH_2$; X_k/X_a, H_2O, 20 °C		no correlation			-0.69 ± 0.03	1.12 ± 0.02	0.795	63.20
X_a/X_k, CH_3OH, 25 °C^d	6.50 ± 0.09	5.52 ± 0.04	0.990	98.01		no correlation		
internal alkenes^e			0.871	75.86		no correlation		

^{a} $\Delta\rho^* = \rho_k^* - \rho_a^*$ or $\rho_a^* - \rho_k^*$, respectively, for oxidation of $R^1R^2C{=}CH_2$ alkenes in aqueous or methanolic medium; $\Delta\rho^* = \rho_k^* - \rho_d^*$ for internal alkenes. ^{b} $(X_k/X_a)_0$, $(X_a/X_k)_0$, and $(X_k/X_d)_0$ for oxidation of $R^1R^2C{=}CH_2$ alkenes in H_2O or CH_3OH and for internal alkenes, respectively. ^{c} Notation is the same as for $\Delta\rho^*$. ^{d} Values of the selectivity calculated from data in ref 6b. ^{e} There are not enough compounds to attempt a correlation slope.
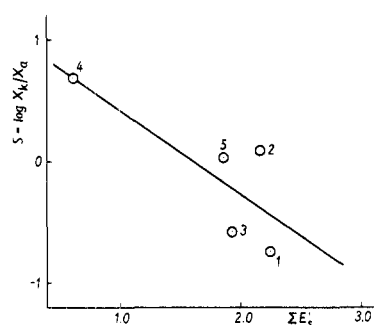

Figure 4. Steric effect on the selectivity (log X_k/X_a) for oxidation of $R^1R^2C{=}CH_2$ alkenes by thallium(III) sulfate at 20 °C. E_s' values are revised Taft steric constants.[17]

Table V. Selectivity Data for the Oxidation of $R^1R^2C{=}CH_2$ Alkenes by $Tl(NO_3)_3$ in Methanol at 25 °C^a

no.	X_a/X_k	X_d/X_c
2	1.65	3.44
3	1.11	3.20
5	0.25	3.62
10^b	0.81	2.73
11^c	2.91	1.38

^{a} Selectivity calculated from the data in ref 6b. ^{b} 2-Methyl-1-hexene. ^{c} 2,3-Dimethyl-1-butene.

selectivities is reversed.[15] The isoselective temperature for oxidation of internal alkenes (T_{is} = 293 K) lies within the range of experimental determination. Whereas 2,4,4-trimethyl-2-pentene (244TMP2) is the most selective of the internal alkenes studied above 293 K [order of selectivity: 244TMP2 > *trans*-4-methyl-2-pentene (t4MP2) > 2-methyl-2-pentene (2MP2)], the selectivities assume the same values in the temperature range 293 ± 10 K (244TMP2 = t4MP2 = 2MP2). Below this temperature 2MP2 is the most selective species (244TMP2 < t4MP2 < 2MP2). Conclusions concerning differences in reactivities or stabilities of the individual alkenes from experimentally available selectivities are possible only if this influence of temperature is observed. The temperature dependence of the selectivity sequence is due to changes in activation enthalpies and entropies which are therefore more suitable experimental data for the interpretation of reaction mechanisms.[14]

Thus the data compiled in Table III and Figures 1–3 show the different changes in selectivity for branched alkenes for intramolecular rearrangements (eq 1 and 2). In accord with the Curtin–Hammett principle,[16] these depend only on the transition-state (TS1, TS2, and TS3) energies. Similarly, it is possible to distinguish between different structures of reactive intermediates.

Structure Effects. The results have been analyzed to provide a quantitative evaluation of the contributions of polar and steric effects to the differences of the free energies of competitive reactions. By using the principle of additivity, we can consider, in the first approximation, the steric and polar effects to be different functions of structure, originating from independent quantities. Results of these relationships are given in Figure 4 and Table IV.

From Table IV it is obvious that steric effects are significant only for oxidation of $R^1R^2C{=}CH_2$ alkenes in

aqueous medium. The data in Table III show that the activation enthalpy, $\Delta H_k^{\ddagger}$, for migration of the bulky alkyl substituents of 244TMP1 becomes favorable relative to $\Delta H_k^{\ddagger}$ for migration of the alkyl ones of 2MB1. Similarly, the steric effects of the alkenes have a considerable influence on the activation entropies (the entropic advantage of intramolecular rearrangements leading to ketones). Our observation is in agreement with the generally adopted conclusion that the migration capability of a substituent increases with its nucleophilicity.[6b,c] There appears to be a general trend toward an increase in selectivity as the ability of the alkyl group to stabilize charge increases. This interpretation is further supported by the observation that a plot of S against $\Sigma E_s'$ gives a relatively significant correlation (Figure 4). Bulky substituents capable of stabilizing the carbocationic species in transition state TS1 (product-determining step of the oxidation) formed during dethallation bring about greater selectivity in these species in accord with the reactivity–selectivity principle.[18]

In the oxidation of α-methylstyrene no formation of the corresponding aldehyde or ethyl phenyl ketone (the latter would be formed by migration of the methyl group) was observed. This fact suggests that the phenyl group migrates much more readily than an alkyl group (in analogy to Wagner–Meerwein's or pinacol rearrangement).

From eq 1 and 2 it is seen that the transition states TS2 and TS3 have very similar structures. According to the Hammond postulate[21] they will also have similar energies. The yield of diol or diether depends on the ability of the external nucleophile to attack the suggested nonclassical carbonium ion before intramolecular rearrangement takes place. This ability will depend on the intrinsic nucleophilicity of the reactant and on steric factors. Bulky substituents at the C_2 atom will hinder the attack of the external nucleophile at the reaction center, and in this manner the intramolecular rearrangements giving carbonyl

(15) When T_{is} is sought, care must be taken that the S is greater than zero. If S is inversed the "inverse selectivity temperature" is found.

(16) For a detailed account of the Curtin–Hammett principle, see, for example, S. I. Miller, *Adv. Phys. Org. Chem.*, **6**, 185 (1968).

(17) J. A. MacPhee, A. Panaye, and J.-E. Dubois, *Tetrahedron*, **34**, 3533 (1978).

(18) For a review of the basis and limitation of the reactivity–selectivity principle, see: (a) ref 13; (b) ref 14; (c) C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975).

(19) R. W. Taft in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, Chapter 13.
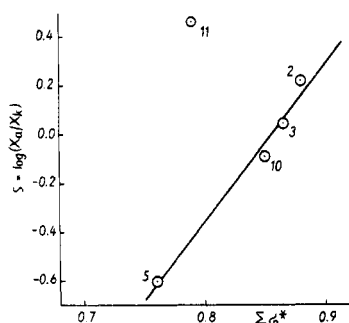
(20) T.-L. Ho, "Hard and Soft Acids and Bases Principle in Organic Chemistry", Academic Press, New York, 1977.

(21) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

Figure 5. Polar effects on the selectivity (log X_a/X_b) for oxidation of $R^1R^2C{=}CH_2$ alkenes by thallium(III) nitrate in methanol at 25 °C. Values of σ^* are from ref 19. 23DMB1 is not included in correlation.

compounds will be favored. This trend may be seen from Tables I, II, and V. For $R^1R^2C{=}CH_2$ alkenes the yield of carbonyl compounds increases with increasing substituent bulk in the order 2MP1 < IB < 2MB1 < αMS < 2EH1 < 244TMP1 (for the oxidation in an aqueous medium, the steric factors dominate) or with increasing nucleophilicity in the order 2-chlorpropene (2CP) < 2EH1 < 2MB1 < 2MP2 < 2MH1 < 2,3-dimethyl-1-butene (23DMB1) (in methanol, the intrinsic nucleophilicity dominates), respectively.

In addition, from Table IV it can be seen that polar effects have influence on selectivity in the oxidation of internal alkenes by thallium(III) sulfate in aqueous medium and in the oxidation of $R^1R^2C{=}CH_2$ alkenes by thallium(III) nitrate in methanol.

Medium Effect. The selectivity data for oxidation of $R^1R^2C{=}CH_2$ alkenes by thallium(III) nitrate in methanol are listed in Table V and illustrated in Figure 5. By comparison of data for aqueous (Table I) and methanolic (Table V) mediums it is obvious that in methanol the product distribution is the reverse of that in water. The slope in Figure 5 has a relatively high absolute value. This is in agreement with direct addition to the C=C bond. The effect on the migration aptitude of alkyl groups, giving

ketones, is decreased with electron-withdrawing substituents, which are suitable for formation of dimethoxy ether. This is the same situation as with the oxidation of terminal n-alkenes.[7b] We propose two possible explanations for this fact. In the simplest terms, we expect the transition state for alkyl group rearrangement (TS1) to be stabilized by an increase in the dielectric constant of the solvent. Thus, in a solvent with a higher dielectric constant (H_2O), formation of ketones would be preferred. It is also possible to interpret the data in terms of the HSAB principle.[20] TS1, TS2, and TS3 are species of nonclassical ion character. According to the HSAB principle, the less carbonium character a center attains during a reaction, the less hard of an acid it will be. Thus, nonclassical carbonium ions are less than hard acids. Methanol is a stronger nucleophilic agent than water (therefore a softer base), so it can better attack the oxythallic adduct with formation of the oxonium ion (TS2 and TS3), thus producing diethers and aldehydes. Simultaneously, electron-withdrawing substituents will decrease electron density at the C_2 atom of TS2, and thus an H^- shift, giving an aldehyde, will be favored. In accord with the reactivity–selectivity principle, the selectivity will be increased.

Conclusion

Oxidation of branched alkenes in aqueous medium gives substantially greater yields of carbonyl compounds than oxidation in methanol. Determination of T_{is} and the "inverse selectivity temperature" has great importance for planning a synthesis of carbonyl compounds and diols or diethers. Mechanistic application of the reactivity–selectivity principle to elucidation of the reaction mechanism of the oxidation of alkenes by thallic salts can lead to serious errors if temperature effects are disregarded.

Reactions of π-Allylic Palladium Intermediates with Amines

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Several dimeric π-allylic palladium chloride complexes have been prepared by addition of aryl-, hydrido-, and (carbomethoxy)palladium chlorides, prepared in situ, to various conjugated dienes. Stoichiometric reactions of several of these complexes with secondary amines were carried out and the influence of added ligands and changes in the anions in the complexes on the reactions were noted. The stoichiometric reactions were then compared to similar catalytic reactions. The evidence suggests that the products formed in the palladium-catalyzed reactions of aryl iodides and bromides with conjugated dienes and secondary amines to form arylated dienes and allylic amines involve π-allylic palladium complexes as intermediates.

The palladium-catalyzed reaction of aryl halides with conjugated dienes and triethylamine produces arylated dienes.[1] The reactions, at least partly, appear to proceed by way of π-allylic palladium complexes which undergo elimination in the final step. π-Allylic palladium complexes are also believed to be intermediates in the palladium-catalyzed reaction of vinylic halides with olefins and amines.[2–4] In many of these reactions the intermediates are resistant to elimination particularly when an aryl,

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